

A Chemical Model of the Troposphere and Stratosphere

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(Manuscript received 8 November 1973, in revised form June 1974)

ABSTRACT

A time-dependent, one-dimensional model of the coupled chemistry and vertical mixing of the atmosphere is used to compute the distribution for many atmospheric constituents of the troposphere and stratosphere. The model treats the photochemistry of the carbon-hydrogen-oxygen-nitrogen system and is (with the exception of H₂O) self-consistent in the sense of requiring no assumptions regarding minor constituent distributions.

1. Introduction

Much of the research on the distribution and effects of minor atmospheric constituents carried on in recent years has been motivated by interest in possible perturbations to the natural atmospheric background that might result from various human activities (Johnson, 1972). A prerequisite to the modeling of such perturbations is a study of the natural background of minor constituents. Because of the great complexity of atmospheric photochemistry such a study should be comprehensive enough to include at least the carbon-hydrogen-oxygen-nitrogen components of the atmosphere and should be self-consistent in the sense of not depending on assumptions regarding the distributions of some of the minor constituents in the model.

The results of several other studies of the vertical distributions of minor atmospheric species have been reported (Whitten and Turco, 1973; Whitten *et al.*, 1973; McConnell and McElroy, 1973; McElroy *et al.*, 1974). This paper describes a time-dependent, one-dimensional model of the coupled chemistry and vertical transport of many of the minor constituents of the atmosphere. The model is computationally similar to that of Whitten *et al.* (1973), the principal differences being the inclusion of the troposphere and lower thermosphere in the present model. Including these regions in the model has the advantages of permitting study of their interaction with the stratosphere, of simplifying the choice of boundary conditions for many constituents, and of lessening the sensitivity of the stratospheric results to the exact choice of boundary conditions.

The models of McConnell and McElroy (1973) and McElroy *et al.* (1974) are computationally quite dif-

ferent from the present model and from that of Whitten *et al.* (1973). Their models are time-independent, and the calculations are more specialized to the physical conditions, such as photochemical equilibrium, appropriate to various constituents at different altitudes. The present calculations, and those of Whitten *et al.*, model the ozone profile throughout the stratosphere while McElroy *et al.* (1974) adopt the observed O₃ concentrations of Hering and Borden (1967) below 28 km. Although dynamics plays the major role in determining the latitudinal distribution of ozone below 30 km, the general features of the global-average vertical distribution can be satisfactorily modeled with a one-dimensional calculation.

The objective of this study is the development of a comprehensive model of the vertical distributions of minor constituents which may be utilized to study their many interactions and which may serve as a basis for further studies of the perturbed atmosphere. The model covers the altitude range 0–170 km, but the results reported here will principally concern the troposphere and stratosphere.

The most important parameters entering into this type of modeling are the set of rate constants, absorption coefficients and quantum yields for those reactions included in the calculations. Intermodel comparison of results is difficult at present due to the diverse sets of data used by various authors. A standard data base is now being developed by investigators at the National Bureau of Standards (Garvin and Hampson, 1973) in support of the Department of Transportation's Climatic Impact Assessment Program (CIAP). The present model utilizes, wherever possible, the data suggested by NBS publications. The overall quantitative and qualitative agreement of the results of these model calculations with available observations of minor constituent dis-

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tributions in the troposphere and stratosphere indicates the general suitability of this data base for atmospheric modeling calculations.

It must be borne in mind that horizontal transport is an important factor in determining the distributions of some minor constituents in the troposphere and stratosphere and care must therefore be exercised in interpreting one-dimensional model calculations. Locally, vertical species distributions may be affected by horizontal-motion-induced vertical transport (Reed and German, 1965) and by variations with time and place in the vertical turbulent diffusivity itself. If transport alone were considered, then one-dimensional models would be appropriate for computing the annual mean of globally-averaged species distributions since transport terms appear linearly in the continuity equations and the horizontal transports would be averaged out of the one-dimensional equations. The difficulty in defining an appropriately averaged species density for a one-dimensional model arises from the nonlinear chemical source terms. Following the usual method of averaging by expressing the species densities as a mean plus a fluctuation results in averages of products of the fluctuation quantities appearing in the continuity equations. These quantities, which follow from the products in the chemical source term, are dropped from the continuity equations in the present model, but this procedure cannot be rigorously justified since they may have non-zero values. Physically, the terms which have been neglected represent changes in the average rate at which chemical reactions among constituents proceed due to transport-induced departures from the mean concentrations. Thus, even though horizontal transport terms can be eliminated from the species continuity equations by appropriate averaging, the effects of horizontal transport are implicit in portions of the nonlinear chemical source terms which have arbitrarily been dropped from consideration. It is in this way that one-dimensional models fail to account for horizontal transport effects. We note that the analogous problem which arises when the continuity equations are averaged over the time scale for turbulent motions has been discussed by Donaldson and Hilst (1972).

We conclude from the above discussion that there is no rigorously defined average species density which present one-dimensional models predict and, in general, only qualitative agreement should be expected even when the results of such models can be compared with globally averaged annual mean densities. We do, of course, expect better agreement for species whose chemical time constants are small relative to lateral transport times since transport-induced departures from the mean should be smallest for such species. Since there are currently not enough data for any species (except possibly ozone) to calculate observed, globally-averaged annual mean densities, model results must usually be compared with data referring

to a particular time and location; here discrepancies due to transport effects may be more pronounced than would be the case if comparison with averaged data were possible.

Despite these limitations of one-dimensional chemical models we find that good qualitative results are often obtained when comparison is made with observed species densities and we believe that such models can usefully be applied to many aeronomic problems. There are several advantages in the use of such models. We can incorporate large numbers of reactions in the chemical source terms and thus study the complex chemical and radiative interactions among the many active atmospheric species in a more self-consistent way than is presently possible with multi-dimensional models. These models can also be used to provide reasonable estimates of the response of the atmosphere to prescribed levels of contaminant loading. Finally, we mention that, because of their relative economy in computation, they can be employed for a wide range of sensitivity studies which can then be used for the effective design of more complex atmospheric models.

2. Theory

a. Basic equations

If the atmosphere contains N unknown constituents, the basic equations to be solved for these are the continuity equations

$$\frac{\partial n_i}{\partial t} = -\frac{\partial \Phi_i}{\partial z} + Q_i(n_j; t), \quad i=1, \dots, N, \quad (1)$$

where n_i and Φ_i are the number density and flux of the i th constituent and $Q_i(n_j; t)$ is the chemical source function. Since Q_i depends on constituents other than the i th and since it contains products of unknown number densities, Eq. (1) comprises a set of N coupled, nonlinear, partial differential equations for the unknown species distributions and must usually be solved numerically. The specific formulation of the terms entering into (1) is given in the following sections. The Appendix contains a discussion of the numerical technique used for their solution.

b. Vertical transport

Eq. (1) expresses the dependence of the species number densities on the chemistry, through the net source term Q_i , and on vertical transport, through the flux divergence $\partial \Phi_i / \partial z$. The vertical flux Φ_i consists, in general, of three parts, a flux due to turbulent motions of the atmosphere (eddy flux), a flux due to molecular diffusion of species i through the background gas, and a flux due to mass motions of the atmosphere as a whole (winds).

The turbulent transport is parameterized in terms of an eddy diffusivity $K(z)$ varying with altitude z ; the eddy flux is written

$$\varphi_{ie}(z) = -K(z) \left[\frac{\partial n_i}{\partial z} + \left(\frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H_m} \right) n_i \right], \quad (2)$$

an equation introduced by Lettau (1951) and extensively employed in one-dimensional models of the atmosphere (e.g., Colegrove *et al.*, 1965; Shimazaki and Laird, 1970). The eddy diffusivity profile must be determined empirically. In (2) T is the temperature and H_m the mean molecular scale height.

The molecular flux for a minor constituent is given by

$$\varphi_{id} = -D_i(z) \left\{ \frac{\partial n_i}{\partial z} + \left[(1 + \alpha_i) \frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H_i} \right] n_i \right\} \quad (3)$$

(Chapman and Cowling, 1961), where H_i and α_i are the molecular scale height and thermal diffusion coefficient; and $D_i(z)$ is the average molecular diffusion coefficient defined by

$$\frac{1}{D_i} = \frac{1}{n_T} \sum_j \frac{n_j}{D_{ij}}, \quad (4)$$

where

$$D_{ij} = - \frac{3}{8\sigma_{ij}^2(n_i + n_j)} \left[\frac{kT(m_i + m_j)}{2\pi m_i m_j} \right]^{1/2} \quad (5)$$

is the mutual diffusion coefficient for constituents i and j , and n_T is the total number density. In (5) k is the Boltzmann constant, σ_{ij} the molecular interaction distance between molecules i and j , and m_i , m_j are the molecular masses. The sum in (4) need only be taken over the major constituents.

The flux due to mass motion of the atmosphere is

$$\varphi_{im} = n_i w_0, \quad (6)$$

where w_0 is the vertical wind component (positive upward). In the present model calculation the vertical velocities are arbitrarily set to zero. Molecular diffusion is negligible compared with eddy diffusion in the troposphere and stratosphere. Molecular flux becomes the dominant transport mechanism above about 110 km.

Substituting the expressions (2), (3) and (6) for the fluxes into (1) results in the following form of the continuity equation:

$$\frac{\partial n_i}{\partial t} = A_i(z) \frac{\partial^2 n_i}{\partial z^2} + B_i(z) \frac{\partial n_i}{\partial z} + C_i(z) n_i + Q_i(n_j; t), \quad (7)$$

where $A_i(z)$, $B_i(z)$ and $C_i(z)$ are coefficients which depend only on the thermal and transport properties of the atmosphere and are thus assumed to be known functions of altitude. Complete expressions for these coefficients are given in Stewart and Hoffert (1973),

and expressions which neglect molecular diffusivities are given in the Appendix.

c. Chemical source term

A general chemical reaction is viewed as a conversion among all the constituents of the model and may be described by an equation of the form

$$\sum_{i=1}^N s'_{ir} n_i \rightarrow \sum_{i=1}^N s''_{ir} n_i, \quad (8)$$

where s'_{ir} and s''_{ir} are the stoichiometric coefficients of the reactants and products, respectively, in the r th reaction. The rate of reaction r is denoted by $k_r(z, t; T)$ which is temperature-dependent in general and for unimolecular photolysis reactions is a function of altitude through the optical depth and of time through the solar flux. The general expression for the net source term in (7) is

$$Q_i(n_j; t) = \sum_{r=1}^M (s''_{ir} - s'_{ir}) k_r(z, t; T) \prod_{j=1}^N n_j^{s'_{jr}}, \quad (9)$$

where M is the number of reactions in the model.

The rate constants in (9) will be specified functions of temperature (and possibly pressure), obtained from laboratory rate measurements, for bimolecular and termolecular reactions, but for unimolecular photolysis reactions they must be computed as functions of altitude from solar flux and molecular absorption cross section data. In this case it is usual to denote the rate coefficient by J_i and we have

$$J_i(z, t) = \sum_{\lambda} f_{\lambda}(t) \sigma_{i\lambda} \eta_{i\lambda} e^{-\tau_{\lambda}(z, t)}, \quad (10)$$

where $f_{\lambda}(t)$ is the solar flux at wavelength λ incident on the top of the atmosphere, $\sigma_{i\lambda}$ the absorption cross section for constituent i at wavelength λ , $\eta_{i\lambda}$ is the photoionization or photodissociation yield for constituent i at wavelength λ , and $\tau_{\lambda}(z, t)$ is the optical depth given by

$$\tau_{\lambda}(z, t) = \text{Ch}[X(z), X(t)] \sum_j \sigma_{j\lambda} \int_z^{\infty} n_j(z') dz', \quad (11)$$

where $\text{Ch}[X, X]$ is the Chapman function (Swider and Gardner, 1967)

$$X(z) = \frac{R+z}{H}, \quad (12)$$

with R the planetary radius, z the altitude and H the local scale height, and $X(t)$ is the solar zenith angle. Neither the time-dependence of the solar flux nor the time-dependence of the solar zenith angle are explicitly included in the present model studies.

TABLE 1. Boundary conditions used in the one-dimensional model.*

Species	Lower boundary		Upper boundary		Reference
	Type	Number density or flux	Type	Number density or flux	
N ₂ O	n	7.2×10^{12}	f	0	Schütz <i>et al.</i> (1970)
NO ₂	n	2.5×10^{10}	p		Robinson and Robbins (1968)
NO	p		p		
H ₂	n	1.3×10^{13}	f	0	Goody (1964)
CH ₄	n	3.7×10^{13}	p		Bainbridge and Heidt (1966)
CO ₂	n	8.3×10^{15}	f	0	Robinson and Robbins (1968)
O ₃	n	7.0×10^{11}	p		<i>Standard Atmosphere Supplements</i>
CO	n	2.8×10^{12}	f	0	Pressman and Warneck (1970)
O	p		f	0	
O(¹ D)	p		p		
O ₂ (¹ Δ _g)	p		p		
N	p		p		
OH	p		p		
H	p		p	0	
NO ₃	p		p		
HO ₂	p		p		
HNO ₂	f	0	p		
CH ₂	p		p		
CH ₂ O ₂	p		f	0	
CH ₃ O	p		f	0	
H ₂ CO	f	0	f	0	
CH ₃ O ₂ H	f	0	f	0	
N ₂ O ₅	p		p		
HNO ₃	f	0	p		
N(² D)	p		p		
H ₂ O ₂	f	0	f		
CHO	p		p	0	

* On the type columns, n stands for a fixed number density, f for a fixed flux, and p for a photochemical equilibrium boundary condition. The references were used in obtaining the number densities at the lower boundary.

The exceptions to the applicability of (10) are dissociation of O₂ in the Schumann-Runge bands and δ-band dissociation of NO. The former are treated using the method and data of Hudson and Mahle (1972) while the latter are treated using Strobel's *J* values for his σ_l absorption coefficients (Strobel, 1971).

d. Boundary conditions

A variety of boundary conditions may be used in the solution of (7) depending on our knowledge concerning a given constituent. A fixed number density at a boundary is the simplest condition if this is known, as it is at the ground for a few constituents. If the number density is unknown but the chemical lifetime is much less than the transport time near the boundary, a photochemical equilibrium boundary condition is appropriate in which the density of a constituent at the boundary on the current time step is estimated from the production and loss terms computed on the previous time step. A specified boundary flux is another alternative.

The general form of the boundary condition used in this model is

$$a_i \frac{\partial n_i}{\partial z} + b_i n_i = c_i(t). \quad (13)$$

The following possibilities are considered:

1. Fixed number density at a boundary

$$a_i = 0, b_i = 1, c_i = \text{constant}. \quad (14)$$

2. Photochemical equilibrium

$$a_i = 0, b_i = l_i(t - \Delta t), c_i = p_i(t - \Delta t), \quad (15)$$

where $l_i(t - \Delta t)$ and $p_i(t - \Delta t)$ are the loss rate per molecule and production rate evaluated at the previous time step.

3. Specified boundary flux

$$a_i = 1, \quad b_i = -\frac{D_i}{D_i + K} \left[(1 + \alpha_i) \frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H_i} \right] + \frac{K}{D_i + K} \left(\frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H_m} \right), \quad (16)$$

$$c_i = \varphi_i$$

where φ_i is the flux at the boundary.

The boundary conditions used in the model are given in Table 1.

3. Data and model input

a. Solar flux and cross-section data

The solar flux data used in these calculations were those compiled by Ackerman (1971) for wavelengths $> 1163 \text{ \AA}$. At shorter wavelengths Hinteregger's (1970) data were used. Cross-section data from a variety of sources were used. These sources are listed in Table 2.

The most important attenuating species insofar as the chemistry of the lower atmosphere is concerned are molecular oxygen and ozone. The cross-section values for the important absorbing wavelengths are shown in Fig. 1, along with the solar ultraviolet flux values above 1300 \AA .

The results reported in this paper are all equilibrium values obtained by using a mean solar intensity. The flux values appropriate at the top of the atmosphere are halved to account for day-night averaging. A solar zenith angle of 57.3° was used which corresponds to the mean daily zenith angle at 30° latitude at equinox.

b. Initial atmosphere

Integration of the continuity equation for the minor atmospheric constituents requires specification of an initial atmosphere. The distribution of the major gases, N₂ and O₂, are taken from the CIRA (1965) mean atmospheric model at altitudes above 80 km. Below this altitude these distributions are computed from the densities given in the 15N annual atmosphere of the *U. S. Standard Atmosphere Supplements* (1966). The water vapor distribution is the mean annual distribution of Sissenwine *et al.* (1968) cited in Wu (1973). Other minor constituents included in the model are assumed to have constant mixing ratios initially.

The temperature profile for the model is taken from

TABLE 2. Photolysis of atmospheric constituents.

Data on reaction	Wavelength interval (Å)	Reference
I. Solar flux	$\lambda > 1163$ $\lambda < 1163$	Ackerman (1971) Hinteregger (1970)
II. Photodissociation		
1. $N_2 + h\nu \rightarrow 2N$		Nicolet (1970)
2. a) $O_2 + h\nu \rightarrow O(^3P) + O(^1D)$	$\lambda < 1750$	Schultz <i>et al.</i> , (1963)
b) $O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	$1750 \leq \lambda \leq 2050$	Hudson and Mahle (1972)
3. a) $O_3 + h\nu \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$	$2050 \leq \lambda \leq 2424$	Ditchburn and Young (1962)
b) $O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^3P)$	$4400 \leq \lambda \leq 8500$	Griggs (1968)
c) $O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D)$	$3100 \leq \lambda \leq 3500$	Griggs (1968)
4. $N_2O + h\nu \rightarrow N_2 + O$	$\lambda < 3100$	Schultz <i>et al.</i> (1963)
5. $NO + h\nu \rightarrow N + O$	$1600 \leq \lambda \leq 2200$	Schultz <i>et al.</i> (1963)
6. $NO_2 + h\nu \rightarrow NO + O$	δ bands	Strobel (1971)
7. $NO_3 + h\nu \rightarrow NO_2 + O_2$	$2850 \leq \lambda \leq 4450$	Leighton (1961)
8. $N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	visible	Schott and Davidson (1958)
9. $H_2O + h\nu \rightarrow H + OH$	$2850 \leq \lambda \leq 3800$	Jones and Wulf (1937)
10. $H_2O_2 + h\nu \rightarrow H_2O + OH$	$200 \leq \lambda \leq 1850$	Schultz <i>et al.</i> (1963)
11. $HO_2 + h\nu \rightarrow OH + O$	$1900 \leq \lambda \leq 2300$	Braun <i>et al.</i> (1972)
12. $HNO_3 + h\nu \rightarrow NO_2 + OH$	$1850 \leq \lambda \leq 2900$	Troe (1973)
13. $HNO_2 + h\nu \rightarrow NO + OH$	$2275 \leq \lambda \leq 2725$	Okabe, H. (1972)
14. $CH_3O_2 + h\nu \rightarrow CH_3O + O$		Assumed equal to (1/37) NO_2 dissociation based on tabulation of Leighton (1961) and assumed unit quantum yield
15. $CH_3OOH + h\nu \rightarrow CH_3O + OH$		Rate adopted after Wofsy <i>et al.</i> (1972)
16. $H_2CO + h\nu \rightarrow HCO + H$ or $H_2 + CO$	$2900 \leq \lambda \leq 3600$	Rate adopted after Wofsy <i>et al.</i> (1972) Calvert <i>et al.</i> (1972)

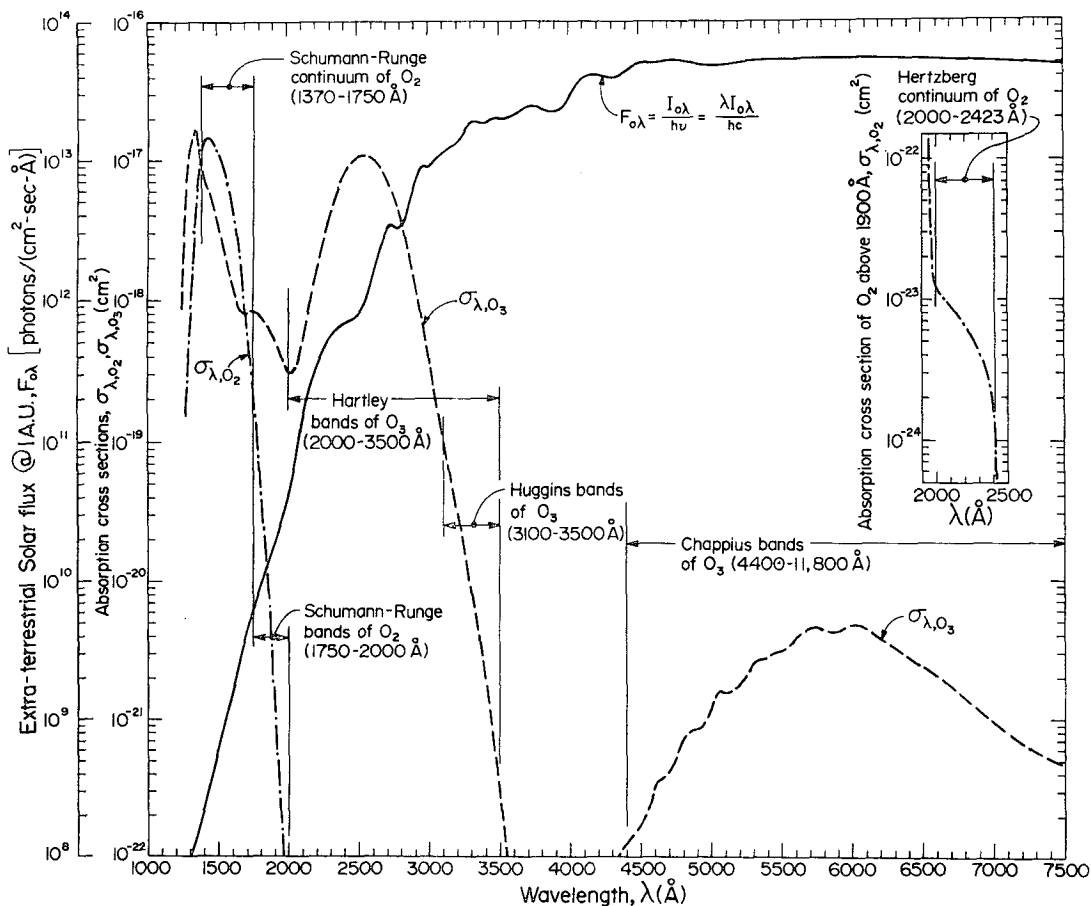


FIG. 1. Oxygen and ozone absorption cross sections and solar ultraviolet flux as a function of wavelength.

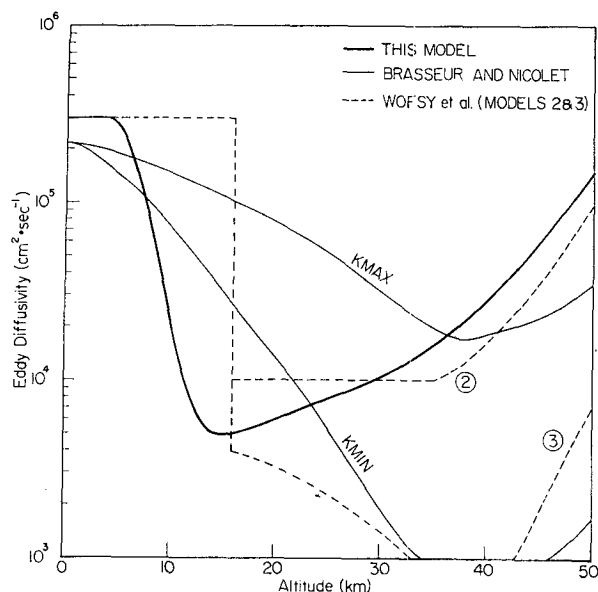


FIG. 2. Eddy diffusivity profile used in the model calculations compared with two employed in the models of Wolfsy *et al.* (1972) and Brasseur and Nicolet (1973).

the same sources as the N_2 and O_2 profiles and is held constant during the computations.

c. Diffusivity data

The eddy diffusivities used in the present model have been obtained from several sources. The $K(z)$ profile from 0 to 50 km is shown in Fig. 2 along with several utilized by other model studies.

4. Results

The neutral species chemical reactions considered in the solution of (7) for the vertical profiles of the unknown constituents are listed in Table 3. Some positive ion reactions were included in the calculations, but these are not pertinent to the photochemistry of the troposphere and stratosphere and are not shown in this table. Since a discussion of the calculated distributions of all the species in the model would be excessively lengthy, only those of greatest interest to the problems of lower atmospheric photochemistry will be considered.

TABLE 3. Reactions and reaction rate coefficients used in the chemical model.

A. Radiative decay		
1.1 $O(^1D) \rightarrow O(^3P) + h\nu$	0.0091	Garstang (1956)
1.2 $O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + h\nu$	0.00028	Badger <i>et al.</i> (1965)
1.3 $N(^2D) \rightarrow N(^4S) + h\nu$	1.1×10^{-5}	Garstang (1956)
B. Quenching		
1.4 $O(^1D) + O_2 \rightarrow O(^3P) + O_2$	7.5×10^{-11}	G^\dagger
1.5 $O(^1D) + N_2 \rightarrow O(^3P) + N_2$	5.5×10^{-11}	G
1.6 $O_2(^1\Delta_g) + O_2 \rightarrow 2O_2$	$2.2 \times 10^{-18} (T/300)^{0.8}$	G
1.7 $O_2(^1\Delta_g) + N_2 \rightarrow O_2 + N_2$	3.0×10^{-21}	Findlay <i>et al.</i> (1969)
1.8 $O_2(^1\Delta_g) + O \rightarrow O_3 + O$	1.0×10^{-16}	Clark and Wayne (1969)
1.9 $O_2(^1\Delta_g) + H_2O \rightarrow O_3 + H_2O$	5.6×10^{-18}	Findley and Snelling (1971)
1.10 $N(^2D) + O \rightarrow N(^4S) + O$	2.0×10^{-13}	Weill (1969)
C. Oxygen reactions		
1.11 $O + O + M \rightarrow O_2 + M$	$3.6 \times 10^{-31} T^{-1} e^{-170/T}$	Schiff (1969)
1.12 $O + O_2 + M \rightarrow O_3 + M$	$1.06 \times 10^{-34} e^{510/T}$	G
1.13 $O + O_3 \rightarrow 2O_2$	$1.9 \times 10^{-11} e^{-2300/T}$	G
1.14 $O(^1D) + O_3 \rightarrow 2O_2$	5.0×10^{-10}	G
1.15 $O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	2.8×10^{-15}	Wayne and Pitts (1969)
D. Hydrogen-oxygen reactions		
1.16 $H + H + M \rightarrow H_2 + M$	$1.2 \times 10^{-32} (273/T)^{0.7}$	Kaufman (1969)
1.17 $H + O_2 + M \rightarrow HO_2 + M$	$2.08 \times 10^{-32} e^{290/T}$	G
1.18 $H + O_2 \rightarrow OH + O_2$	2.6×10^{-11}	G
1.19 $H + HO_2 \rightarrow H_2O + O$	$8.0 \times 10^{-12} e^{-500/T}$	Lloyd (1971)
1.20 $H + HO_2 \rightarrow H_2 + O_2$	$4.2 \times 10^{-11} e^{-350/T}$	G
1.21 $H + HO_2 \rightarrow 2OH$	$4.2 \times 10^{-10} e^{-950/T}$	G
1.22 $H_2 + O(^1D) \rightarrow H + OH$	2.9×10^{-10}	G
1.23 $H_2 + OH \rightarrow H + H_2O$	$6.8 \times 10^{-12} e^{-2000/T}$	Greiner (1969)
1.24 $OH + O \rightarrow H + O_2$	4.2×10^{-11}	G
1.25 $OH + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} e^{-1000/T}$	G
1.26 $OH + OH \rightarrow H_2O + O$	$1.0 \times 10^{-11} e^{-550/T}$	G
1.27 $OH + HO_2 \rightarrow H_2O + O_2$	$1.6 \times 10^{-11} e^{-500/T}$	Lloyd (1971)
1.28 $OH + H_2O_2 \rightarrow H_2O + HO_2$	$1.7 \times 10^{-11} e^{-910/T}$	G
1.29 $H_2O + O(^1D) \rightarrow 2OH$	3.5×10^{-10}	G
1.30 $HO_2 + O \rightarrow OH + O_2$	$8.3 \times 10^{-11} e^{-500/T}$	Lloyd (1971)
1.31 $HO_2 + O_3 \rightarrow OH + 2O_2$	$1.0 \times 10^{-13} e^{-1250/T}$	G
1.32 $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$3.0 \times 10^{-11} e^{-500/T}$	G
1.33 $H_2O_2 + O \rightarrow OH + HO_2$	$3.6 \times 10^{-11} e^{-2950/T}$	G

TABLE 3 (continued).

E. Nitrogen-oxygen reactions		
1.34 $N+O_2 \rightarrow NO+O$	$1.1 \times 10^{-14} e^{-3150/T}$	G
1.35 $N+O_3 \rightarrow NO+O_2$	5.7×10^{-13}	G
1.36 $N+NO \rightarrow N_2+O$	2.7×10^{-11}	G
1.37 $N(^2D)+O_2 \rightarrow NO+O$	6.0×10^{-12}	Black <i>et al.</i> (1969)
1.38 $N_2O+O(^1D) \rightarrow 2NO$	1.1×10^{-10}	G
1.39 $N_2O+O(^1D) \rightarrow N_2+O_2$	1.1×10^{-10}	G
1.40 $NO+O+M \rightarrow NO_2+M$	$4.0 \times 10^{-32} e^{840/T}$	G
1.41 $NO+O_3 \rightarrow NO_2+O_2$	$9.0 \times 10^{-13} e^{-1200/T}$	G
1.42 $NO+NO_3 \rightarrow 2NO_2$	2.0×10^{-11}	G
1.43 $NO_2+O \rightarrow NO+O_2$	9.1×10^{-12}	G
1.44 $NO_2+O+M \rightarrow NO_3+M$	1.0×10^{-31}	G
1.45 $NO_2+O_3 \rightarrow NO_3+O_2$	$6.3 \times 10^{-12} e^{-3500/T}$	G
1.46 $NO_2+NO_3+M \rightarrow N_2O_5+M$	$1.0 \times 10^{-22}/(1.7 \times 10^{-10}[M]+2 \times 10^8)$	Whitten and Turco (1973)
1.47 $N_2O_5+M \rightarrow NO_2+NO_3+M$	$8.3 \times 10^{-8} e^{-8300/T}$	Bahn (1968)
F. Nitrogen-hydrogen-oxygen reactions		
1.48 $NO+OH+M \rightarrow HNO_2+M$	$6.0 \times 10^{-31} (300/T)^3$	Anderson and Kaufman (1972)
1.49 $NO+HO_2 \rightarrow NO_2+OH$	2.0×10^{-13}	G
1.50 $NO_2+OH+M \rightarrow HNO_3+M$	$2.8 \times 10^{-22}/(4 \times 10^{-14}[M]+4.87^3)$	Whitten and Turco (1973)
1.51 $OH+HNO_3 \rightarrow H_2O+NO_3$	1.3×10^{-13}	G
1.52 $OH+HNO_2 \rightarrow H_2O+NO_2$	1.3×10^{-13}	estimate
1.53 $HNO_3+O \rightarrow OH+NO_3$	1.5×10^{-14}	G
1.54 $HNO_2+O \rightarrow OH+NO_2$	1.5×10^{-14}	estimate
G. Inorganic carbon reaction		
1.55 $CO+OH \rightarrow CO_2+H$	1.33×10^{-13}	G
H. Organic carbon reactions		
1.56 $CH_4+O \rightarrow CH_3+OH$	$3.5 \times 10^{-11} e^{-4550/T}$	G
1.57 $CH_4+O(^1D) \rightarrow CH_3+OH$	4.0×10^{-10}	G
1.58 $CH_3+O \rightarrow H_2CO+H$	3.0×10^{-13}	Nicolet (1971)
1.59 $CH_3+O_2 \rightarrow H_2CO+OH$	3.0×10^{-16}	G
1.60 $CH_3+O_2+M \rightarrow CH_3O_2+M$	2.6×10^{-31}	G
1.61 $CH_3O+O_2 \rightarrow H_2CO+HO_2$	$1.6 \times 10^{-13} e^{-3300/T}$	G
1.62 $HCO+O_2 \rightarrow CO+HO_2$	1.7×10^{-13}	G
1.63 $CH_4+OH \rightarrow CH_3+H_2O$	$4.77 \times 10^{-11} e^{-2500/T}$	G
1.64 $H_2CO+OH \rightarrow HCO+H_2O$	1.6×10^{-13}	G
1.65 $H_2CO+HO_2 \rightarrow H_2O_2+HCO$	$8.0 \times 10^{-12} e^{-3250/T}$	Lloyd (1971)
1.66 $CH_3OOH+OH \rightarrow CH_3O_2+H_2O$	9.4×10^{-13}	Levy (1972)
1.67 $CH_3O_2+HO_2 \rightarrow CH_3OOH+O_2$	6.7×10^{-14}	G
1.68 $CH_3O_2+NO \rightarrow CH_3O+NO_2$	5.0×10^{-13}	Levy (1972) [estimated]

† Refers to Garvin (1973).

a. Ozone

Fig. 3 shows the computed vertical profile of atmospheric ozone between 0 and 50 km. The magnitude of the peak ozone density and the total amount in a vertical column, about 240 Dobson units, are well within the range of observed values. The altitude of the maximum is, at 28 km, somewhat higher (2–6 km) than the observed range. Ozone distributions given by Wu (1973) are shown for comparison. The discrepancy between observed and calculated altitudes of the ozone maximum is probably due to the inadequate dynamics of the model. The most likely explanation for the discrepancy between calculated and observed peak ozone densities is that the NO_x densities predicted by the model in the 10–18 km altitude region are too high. There is downward transport of ozone below 30 km in the model and an O_3 flux into the region of excessive NO_x concentrations results in a lowering of calculated O_3 densities at higher altitudes. A comparison between computed and observed odd-nitrogen constituents will be given below.

The principal ozone production and loss rates are shown as function of altitude in Fig. 4. Photodestruc-

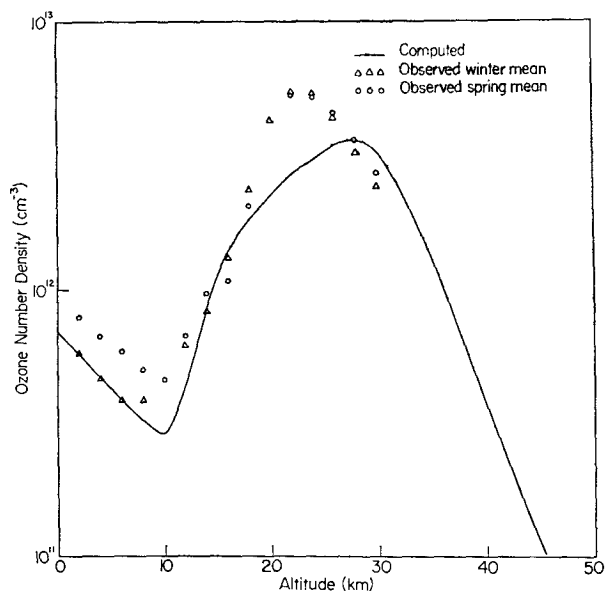


FIG. 3. Computed ozone distribution compared with observed mean values.

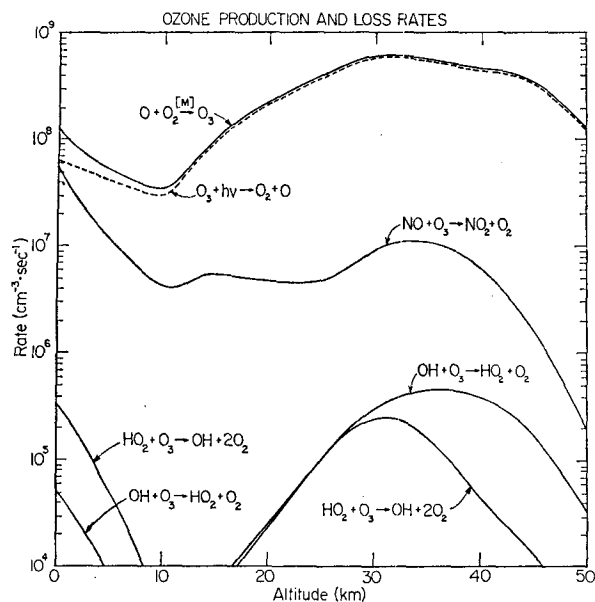


FIG. 4. Ozone reaction rates.

tion of ozone is closely balanced by the three-body association $O + O_2 + M \rightarrow O_3 + M$ throughout most of the stratosphere. Destruction of ozone by odd nitrogen (NO) is clearly more important than destruction by odd hydrogen (OH and HO_2) throughout the lower atmosphere. Reactions which convert O_3 to O are not shown on Fig. 4 since they lead to negligible net loss of ozone.

b. Distribution of odd nitrogen

The computed mixing ratios of the most abundant odd-nitrogen species, NO, NO_2 and HNO_3 , are shown in Fig. 5 and compared with various observations. The dashed lines are observed nitric acid mixing ratios taken from the graphical data of Williams *et al.* (1972) and Murray *et al.* (1973). The calculated profile is comparable in magnitude with these observations. The nitrogen dioxide abundances observed by Ackerman and Muller (1972) are shown by closed circles with error bars. Except for the lowest and highest points these agree well with the computed NO_2 mixing ratio. As noted by Ackerman and Muller (1972) the lowest point is probably in the troposphere, but the observed abundance of 3.4 ± 1 ppb is greater than the tropospheric abundances of the model. The latter are undoubtedly influenced by the fixed abundance of NO_2 (1 ppb) at ground level. The sharp (factor of 2) decrease in NO_2 mixing ratio in a 1-km interval implied by the highest point in Ackerman and Muller's data is not replicated by the model, but the existence of a stratospheric NO_2 layer indicated by the trend of the data is seen in the calculated profiles. Nitric oxide is the least abundant form of odd nitrogen throughout most of the region below 40 km. Above

20 km the computed NO mixing ratios are in reasonable agreement with the observations of Ackerman *et al.* (1973); however, as noted above, computed NO densities appear to be too large between 10–18 km in the model. At 16.5 km Ackerman *et al.* observe 0.07 ppb NO, about a factor of 4 less than that computed in the model. The observations of Schiff (1973) near 13 km also indicate about a factor of 4 less NO than computed with the model. We cannot at present explain this discrepancy between calculated and observed NO mixing ratios in the lower stratosphere.

The most important point to be made with regard to these mixing ratios is the preponderance of nitric acid in the lower stratosphere. This may have implications for the problem of stratospheric contamination due to NO_x injection by high-altitude aircraft. If the relatively inert nitric acid provides a significant reservoir for the injected NO_x then the effective aircraft emissions would be less than might be inferred from measured engine emissions indices. The reduction of stratospheric ozone resulting from such contamination would be less than that predicted by model calculations which omit HNO_3 chemistry.

Similar remarks apply to the possible role of nitrous acid in the stratosphere. HNO_2 profiles have been computed in the present model, but are not discussed in detail since the production and loss rates for HNO_2 are much less certain than those for HNO_3 and there are no observations for comparison.

The only source of odd nitrogen considered in the lower atmosphere is the reaction $N_2O + O(^1D) \rightarrow 2NO$.

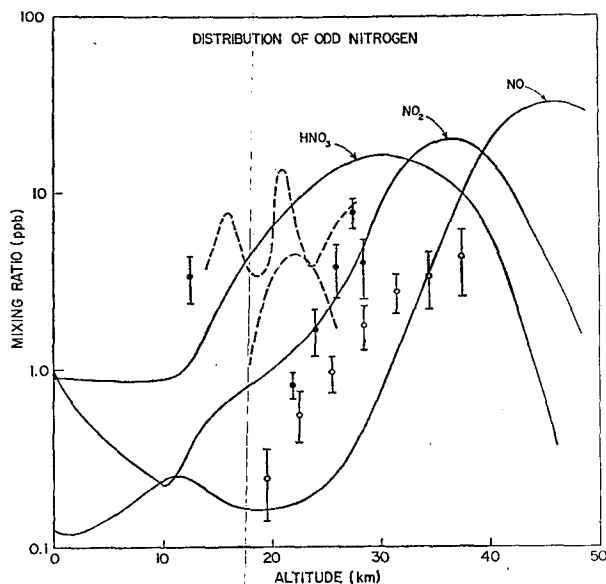


FIG. 5. Calculated distributions of odd nitrogen in the lower atmosphere and comparisons with data. Dashed lines, observed HNO_3 mixing ratios of Williams *et al.* (1972) and Murray *et al.* (1973); closed circles, observed NO_2 mixing ratios of Ackerman and Muller (1972); open circles, observed NO mixing ratios of Ackerman *et al.* (1973).

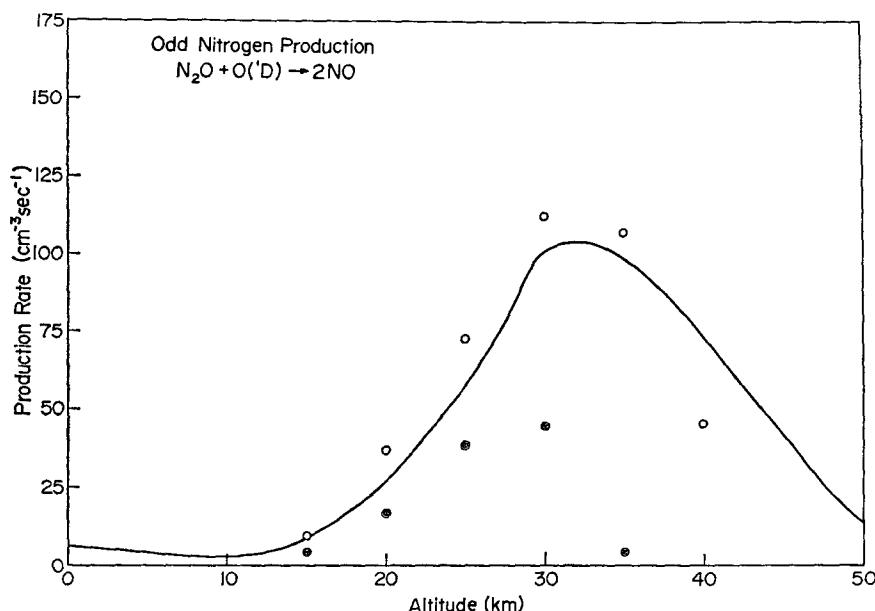


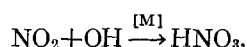
FIG. 6. Odd nitrogen production rate and comparison with maximum (open circles) and minimum (closed circles) rates from the model of Brasseur and Nicolet (1973).

The computed production rate is shown in Fig. 6 and compared with the maximum and minimum rate calculated by Brasseur and Nicolet (1973).

There are no major sinks of odd nitrogen in the stratosphere. The layered structure exhibited by the various species is primarily determined by reactions which convert one form of odd nitrogen to another. Production and loss rates for HNO_3 are shown in Fig. 7. The only production of nitric acid in the model results from reactions of NO_2 with OH to form HNO_3 . This is nearly balanced throughout most of the stratosphere by photodissociation. Chemical loss of HNO_3 by reaction with either O or OH is negligible below about 35 km though oxidation by O is important at higher altitudes. The computed HNO_3 concentration departs substantially from the photochemical equilibrium value

$$\frac{[\text{HNO}_3]}{[\text{NO}_2]} = \frac{k_1[\text{OH}][\text{M}]}{J_1}, \quad (17)$$

where k_1 is the rate coefficient for



and J_1 the HNO_3 photodissociation coefficient. This reflects the fact that the chemical lifetime of nitric acid is relatively long in the stratosphere and transport plays an important role in establishing its distribution.

At altitudes above 40 km NO is the principal form of odd nitrogen due to the increasingly rapid reduction of NO_2 via the reaction $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$. The de-

crease in NO mixing ratio above 45 km results from δ -band dissociation.

The distribution of nitrogen dioxide is generally similar to that of the odd-nitrogen production rate. At higher altitudes there is a fall-off in the NO_2 mixing ratio due to the aforementioned reduction by atomic oxygen while at lower altitudes conversion to nitric acid is increasingly important. The reaction converting NO to NO_2 and NO_2 to NO are rapid enough for the ratio of the concentrations $[\text{NO}_2]/[\text{NO}]$ to attain its

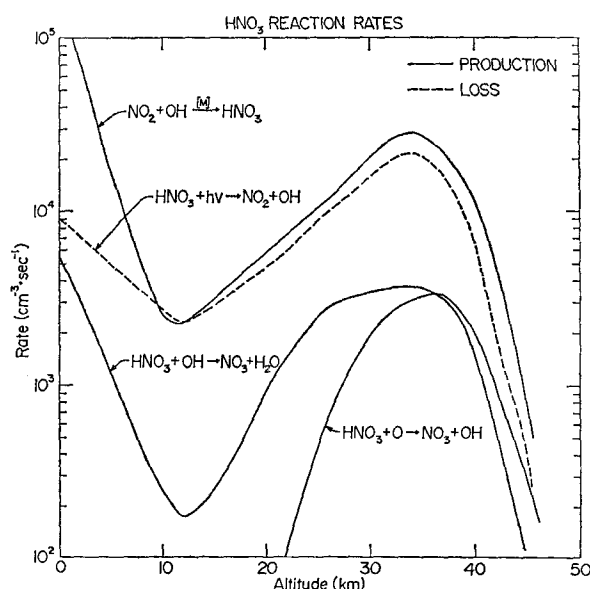


FIG. 7. Computed nitric acid reaction rates.

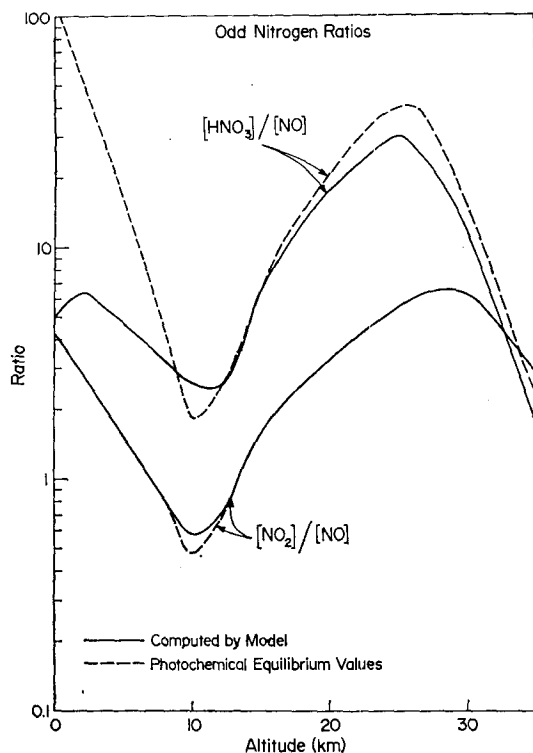


FIG. 8. Calculated ratios of $[\text{HNO}_3]/[\text{NO}]$ and $[\text{NO}_2]/[\text{NO}]$ and comparison with their photochemical equilibrium values.

photochemical equilibrium value throughout the lower atmosphere. It is easy to show that this ratio is given by

$$[\text{NO}_2]/[\text{NO}] = \frac{k_2[\text{O}_3]}{J_2 + k_3[\text{O}]} \quad (18)$$

(see, e.g., Brasseur and Nicolet, 1973), where k_2 and k_3 are the rate coefficients for the reactions $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ and $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$, respectively, and J_2 is the NO_2 photodissociation coefficient. The ratios $[\text{HNO}_3]/[\text{NO}]$ and $[\text{NO}_2]/[\text{NO}]$ computed by the model are shown in Fig. 8 along with the photochemical equilibrium values of these ratios computed from (17) and (18).

b. Distributions of CH_4 , H_2 , N_2O

These constituents are relatively inert in the lower atmosphere. Their chemical time constants are long and their distributions are thus sensitive to the assumed values of the eddy diffusion profile. Comparison of computed and observed values for these constituents are most useful in deciding on appropriate values of eddy diffusivity throughout the stratosphere. Departure from constant mixing ratios which occurs in the stratosphere are primarily due to attack by $\text{O}(^1\text{D})$ and OH [OH and $\text{O}(^1\text{D})$ destruction of CH_4 and H_2 are comparable in the stratosphere], though

there is evidence of an H_2 source in the lower stratosphere (Ehhalt and Heidt, 1973).

Fig. 9 shows the computed distributions of these constituents and compares them with various observations. The mixing ratio of N_2O is held fixed at the ground at a value of 0.28 ppm, consistent with the observation of Schütz *et al.* (1970), but somewhat lower than those of Goody (1969) or Goldman *et al.* (1973). Both the observations reported by Schütz *et al.* and Goldman *et al.* indicate a more rapid decrease in the N_2O mixing ratio above the tropopause than is shown in the present model or in the mixing ratio curves computed by Nicolet and Peetermans (1972).

The computed H_2 mixing ratio shows a smaller maximum between 20–30 km than do the data of Ehhalt and Heidt (1973). A likely source of H_2 in the stratosphere is photolysis of formaldehyde, $\text{H}_2\text{CO} + h\nu \rightarrow \text{H}_2 + \text{CO}$. The computed distribution of formaldehyde has a maximum at about 30 km which is consistent with an H_2 peak in the same region, but the magnitude of the H_2CO maximum is too small in the model to produce such an H_2 peak.

The CH_4 mixing ratio, like that of H_2 , drops off more rapidly in the model than do the observed ratios of Ehhalt and Heidt. This indicates the need for an upward revision of the stratospheric K values used above 30 km.

c. Distributions of free radicals

The free radical species OH , HO_2 and CH_3O_2 play an important role in the chemistry of the troposphere and stratosphere, but since they are highly reactive their concentrations are low and there are no direct observations with which to compare calculated results.

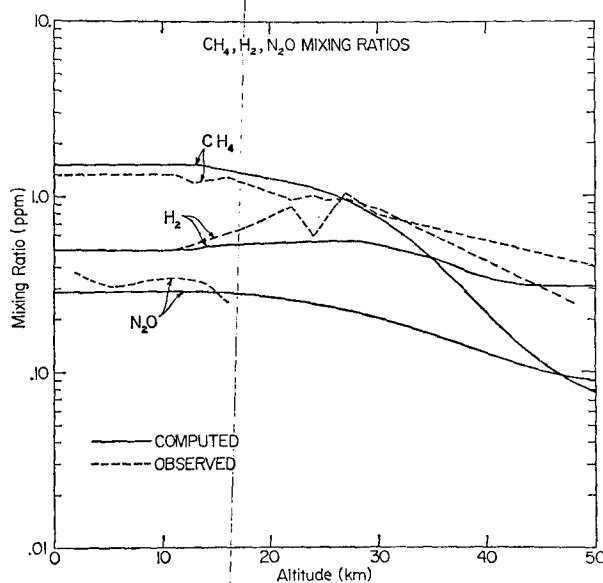


FIG. 9. Computed distributions of methane, hydrogen and nitrous oxide and comparison with observations.

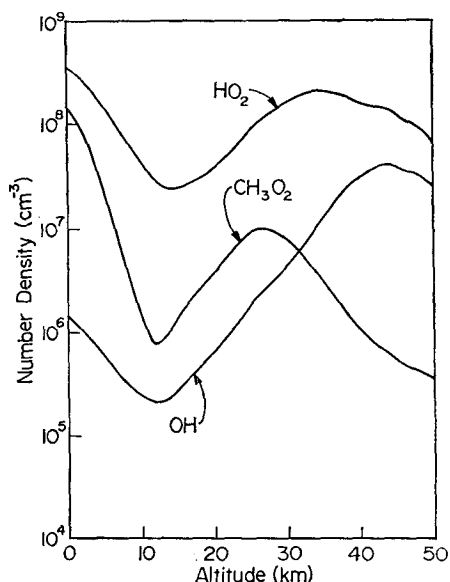


FIG. 10. Computed distributions of free radicals, HO_2 , OH and CH_3O_2 .

The theoretical distributions of these species are shown in Fig. 10.

The presence of all of these species in the troposphere and stratosphere is due to the photolysis of ozone, producing $\text{O}(^1\text{D})$ which in turn generates OH by attacking H_2O , CH_4 and H_2 . The important production and loss processes for these species are shown in Figs. 11, 12 and 13. Since water vapor is much

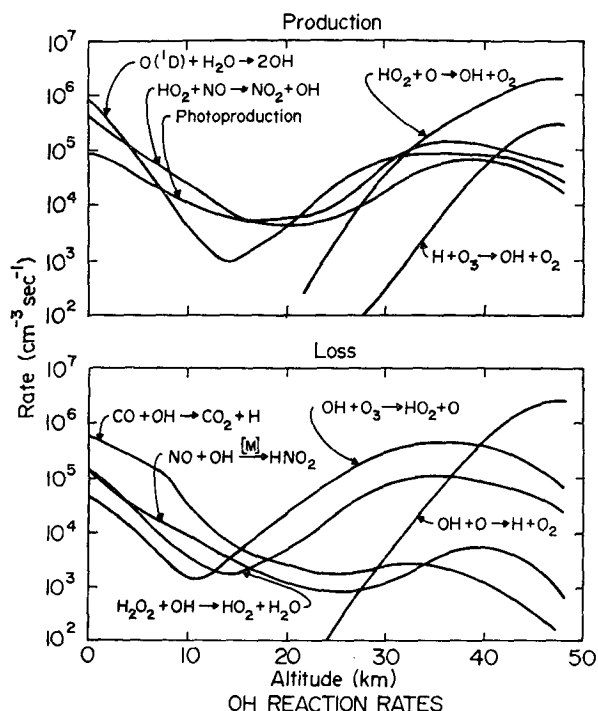


FIG. 11. Computed hydroxyl radical reaction rates.

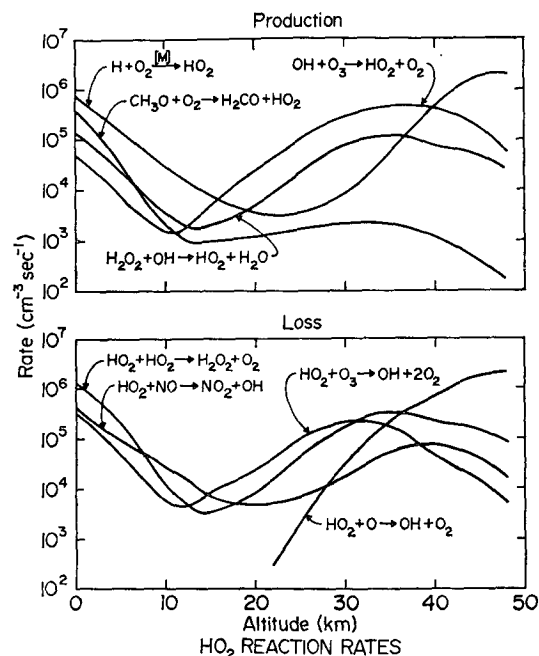


FIG. 12. Computed hydroperoxy radical reaction rates.

more abundant than methane or hydrogen below 50 km, it serves as the primary source for production of hydroxyl radicals.

The hydroxyl radical is the primary source of the hydroperoxy radical throughout the lower atmosphere. Below 16 km HO_2 is produced in a two-step process beginning with the oxidation of carbon monoxide, $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$, followed immediately by $\text{H} + \text{O}_2$

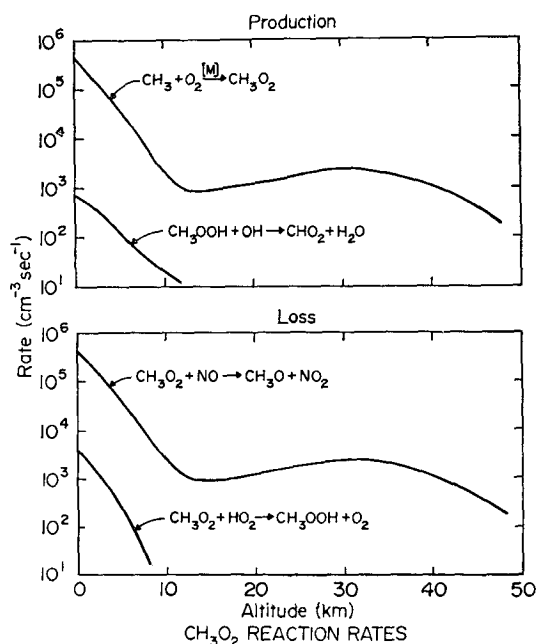


FIG. 13. Computed methylperoxy radical production and loss rates.

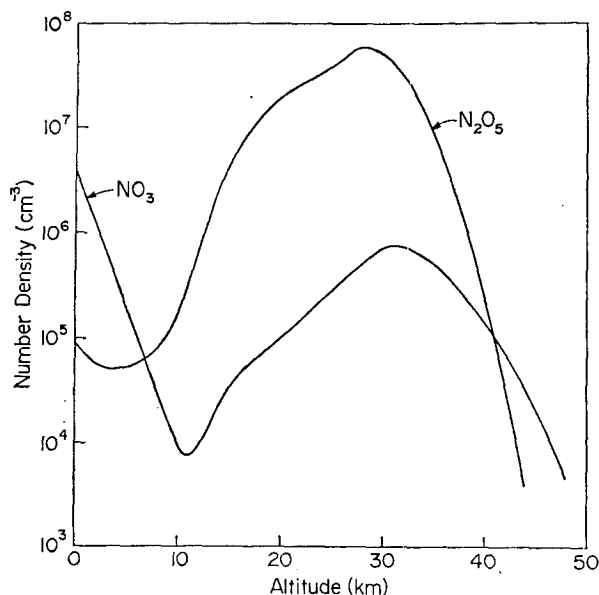


FIG. 14. Computed distributions of nitrogen trioxide and nitrogen pentoxide.

$+M \rightarrow HO_2 + M$. Between 16 and 40 km direct oxidation by ozone, $OH + O_3 \rightarrow HO_2 + O_2$, is the principal hydroperoxy source. Above 40 km a two-step process involving the three-body reaction with atomic hydrogen and oxygen is again the major HO_2 source, but at these altitudes $OH + O \rightarrow H + O_2$ is the atomic hydrogen source.

The loss of odd hydrogen occurs via the formation of constituents such as H_2O_2 , HNO_3 and HNO_2 and subsequent rainout, or via chemical reactions such as $HNO_3 + OH \rightarrow H_2O + NO_3$ which lead to water vapor as a product.

d. Distribution of other species of interest

A small amount of the odd nitrogen in the lower atmosphere resides in the more highly oxidized form NO_3 and N_2O_5 whose computed distributions are shown in Fig. 14. These constituents provide a small and temporary reservoir for odd nitrogen and do not lead to significant loss or production of HNO_2 or HNO_3 .

The computed distributions of H_2O_2 , CH_3O_2H and H_2CO are shown in Fig. 15. Hydrogen peroxide is produced solely by the three-body reaction $2HO_2 + M \rightarrow H_2O_2 + M$ and lost by rainout and by reaction with OH . Methyl hydroperoxide and formaldehyde are two of the products formed from the oxidation of methane.

5. Summary and conclusions

An almost fully self-consistent one-dimensional model of the atmosphere has been utilized to calculate the distributions of minor constituents in the troposphere

and stratosphere. Water vapor is the sole exception to the requirement that all minor constituents (i.e., other than N_2 and O_2) be treated as variables to be computed from the coupled set of species continuity equations. The reason for the exception is that the model is not designed to treat condensable vapors.

The calculations presented in this paper have shown the feasibility of using a one-dimensional model employing a single mathematical technique to describe the vertical distributions of minor atmospheric constituents. Stiffness is not a fundamental constraint on obtaining solutions of the continuity equations though considerable computing power is required for the investigation of large chemical systems.

The limitations imposed on the model results by the exclusion of lateral transport from the calculations have been discussed in the Introduction. The severity of the constraints imposed on the utility of a one-dimensional model by the assumptions implicit in its formulation can only be judged *a posteriori* by comparison of calculated results with the few observations presently available. We believe the generally satisfactory agreement of the present model results with observations shows that it may usefully be employed to study the multitude of interactions between the various chemical species in the atmosphere and to model the response of the stratosphere to man-made perturbations.

Acknowledgments. We are indebted to Ms. Clair Ambler of the Computer Sciences Corporation (CSC) staff for her able programming of the calculations. Dr. C. Weng of CSC was helpful in developing efficient techniques for performing several of the com-

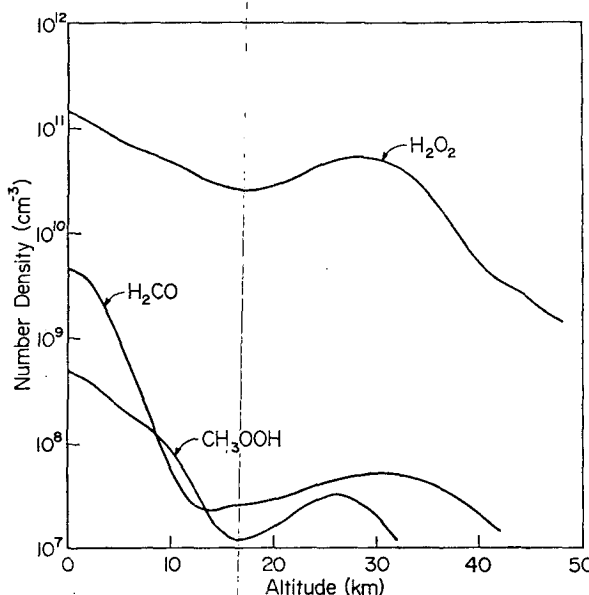


FIG. 15. Computed distributions of hydrogen peroxide, methylhydroperoxide and formaldehyde.

putations. One of us (M.H.) was supported by a National Academy of Sciences—National Research Council Senior Research Associateship.

APPENDIX

Numerical Methods

1. Stability and accuracy

The simplest approach to solving Eq. (7) for the number densities n_i would be to adopt a standard differencing scheme and linearize $Q_i(n_j; t)$ by evaluating n_j at $t - \Delta t$. For reasonable values of Δt such an approach quickly becomes unstable as manifested by the calculation of negative number densities. The source of the instability is the very small chemical time constants implicit in the source term Q_i and not the type of difference scheme employed. Eq. (7) exhibits "stiffness" (Gelinas, 1972).

The constraint on Δt is readily estimated if transport is neglected and a typical continuity equation written, i.e.,

$$\frac{dn_i}{dt} = Q_i(n_j; t). \quad (\text{A1})$$

The forward difference solution for n_i on the $(k+1)$ th time step is

$$n_i^{k+1} = n_i^k + Q_i(n_j^k; t)\Delta t, \quad (\text{A2})$$

where superscripts refer to the time step. We thus require

$$\Delta t \ll \left| \frac{n_i}{Q_i(n_j; t)} \right|, \quad (\text{A3})$$

which can constrain Δt to the sub-microsecond range in a system with very reactive constituents.

The stiffness of Eq. (7) may be handled in various ways. The space derivatives may be written at the outset in differenced form and the continuity equations treated as a set of ordinary differential equations for the number densities as functions of time (Chang *et al.*, 1973). Any of several techniques for handling stiff ordinary differential equations may then be employed. Alternatively, the most reactive constituents may be calculated from the assumption that they are in photochemical equilibrium. Different numerical techniques are thus used for different constituents and in some cases for a single constituent in different altitude ranges (Wofsy *et al.*, 1972). In terms of computing time this is probably the most efficient approach, but it requires specialization to the particular chemical system under investigation.

Our approach to the stiffness problem is to resolve the net source term into production and loss components for each constituent (as is done in most model calculations) and use an implicit difference scheme to solve the resulting continuity equation (see Shimazaki,

1972). With the same approximation used in (A1) the continuity equations are

$$\frac{dn_i}{dt} = -l_i(n_j)n_i + p_i(n_j), \quad (\text{A4})$$

where

$$l_i(n_j) = \sum_{r=1}^M |s_{ir}| k_r(z, t; T) \prod_{j=1}^{N-1} n_j^{s_{jr}}, \quad (\text{A5})$$

$$p_i(n_j) = \sum_{r=1}^M s_{ir} k_r(z, t; T) \prod_{j=1}^N n_j^{s_{jr}}, \quad (\text{A6})$$

where $s_{ir} = s'_{ir} - s''_{ir}$ is the net stoichiometric coefficient for the i th constituent in reaction r and the other quantities are defined in relation to Eqs. (8) and (9) in the text. The implicit difference solution of (A4) is

$$n_i^{k+1} = \frac{n_i^k + p_i(n_j^k)\Delta t}{1 + l_i(n_j^k)\Delta t}. \quad (\text{A7})$$

Since the right hand side of (A7) is always positive the solution is stable and the problem of stiffness is alleviated. Solutions of the continuity equations (A4) are in fact stable for all values of Δt . For $l_i(n_j^k)\Delta t \gg 1$, (A7) reduces to the photochemical equilibrium solution

$$n_i^{k+1} \approx \frac{p_i(n_j^k)}{l_i(n_j^k)}. \quad (\text{A8})$$

As has been noted by several authors (Shimazaki, 1972; Whitten *et al.*, 1973) solutions of the continuity equations must be accurate as well as stable. Our approach to insuring accuracy is to evaluate the nonlinear source and loss terms iteratively within each time step. In terms of the simplified equation (A4) our solution would be

$$n_i^{k+1} = \frac{n_i^k + p_i(n_j^{k+\frac{1}{2}})\Delta t}{1 + l_i(n_j^{k+\frac{1}{2}})\Delta t}, \quad (\text{A9})$$

where $n_j^{k+\frac{1}{2}}$ are the number densities evaluated iteratively at the mid-interval $(t + \frac{1}{2}\Delta t)$ in time, i.e.,

$$n_i^{k+\frac{1}{2}} = \frac{1}{2}[n_i^{k+1} + n_i^k]. \quad (\text{A10})$$

The numerical scheme

$$n_i^{k+1} = \frac{n_i^k + p_i(n_j^{k+1})\Delta t}{1 + l_i(n_j^{k+1})\Delta t} \quad (\text{A11})$$

does not converge. As noted by Whitten *et al.* (1973) an iterative scheme such as (A9) requires about 10 iterations to assume adequate accuracy. The unknowns $n_i^{k+\frac{1}{2}}$ converge at different rates, however, and this statement applies only to the most slowly converging. In practice, most of the number densities $n_i^{k+\frac{1}{2}}$ have

converged after three or four iterations and this fact may be used to speed the computational procedure.

2. Finite-difference scheme

The method applied to the solution of Eq. (7) is the Crank-Nicholson implicit difference scheme (Smith, 1965). The time derivative is replaced by its forward difference

$$\frac{\partial n}{\partial t} \rightarrow \frac{n_{i,j+1} - n_{i,j}}{\Delta t}, \quad (\text{A12})$$

where index i now refers to the spatial coordinate z , and j refers to the time. The index referring to the identity of the species has been dropped. The space derivatives are replaced by the mean of their central differences on the $(j+1)$ th and j th time rows:

$$\frac{\partial^2 n}{\partial z^2} \rightarrow \frac{n_{i+1,j+1} - 2n_{i,j+1} + n_{i-1,j+1}}{2(\Delta z)^2} + \frac{n_{i+1,j} - 2n_{i,j} + n_{i-1,j}}{2(\Delta z)^2}, \quad (\text{A13})$$

$$\frac{\partial n}{\partial z} \rightarrow \frac{n_{i+1,j+1} - n_{i-1,j+1}}{4\Delta z} + \frac{n_{i+1,j} - n_{i-1,j}}{4\Delta z}. \quad (\text{A14})$$

The loss term $l_i(n_j)$ defined by (A5) is incorporated into the coefficient $c_i(z)$ of the continuity equations (7) which are then written

$$\frac{\partial n_i}{\partial t} = A_i(z) \frac{\partial^2 n_i}{\partial z^2} + B_i(z) \frac{\partial n_i}{\partial z} + C_i(z; n_j) n_i + p_i(n_j), \quad (\text{A15})$$

where $p_i(n_j)$ is defined in (A6), and

$$\left. \begin{aligned} A_i(z) &= K(z) \\ B_i(z) &= K(z) \left[\frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H_m} \right] + K'(z) - w_0 \\ C_i(z; n_j) &= K(z) \left[\frac{\partial^2 \ln T}{\partial z^2} - \frac{\beta_m}{H_m^2} \right] \\ &\quad + K'(z) \left[\frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H_m} \right] - \frac{\partial w_0}{\partial z} + l_i(n_j) \end{aligned} \right\}; \quad (\text{A16})$$

$K'(z)$ is the derivative of the eddy diffusivity with respect to altitude, β_m is the gradient of the mean molecular scale height, and the other quantities are defined in the text. Defining

$$\left. \begin{aligned} r &= \frac{\Delta t}{(\Delta z)^2} \\ s &= \frac{\Delta t}{\Delta z} \end{aligned} \right\}, \quad (\text{A17})$$

and substituting the finite-difference approximations (A12)–(A14) into (A15), we have the following set of equations for each constituent:

$$-a_i n_{i+1} + n_i - c_i n_{i-1} = d_i, \quad (\text{A18})$$

where

$$\left. \begin{aligned} a_i &= (1 + rA_i - \Delta t c_i)^{-1} \left(\frac{r}{2} A_i + \frac{s}{4} B_i \right) \\ c_i &= (1 + rA_i - \Delta t c_i)^{-1} \left(\frac{r}{2} A_i - \frac{s}{4} B_i \right) \\ d_i &= (1 + rA_i - \Delta t c_i)^{-1} \\ &\quad \times \left[\left(\frac{r}{2} A_i + \frac{s}{4} B_i \right) n_{i+1,j} + (1 - rA_i) n_{i,j} \right. \\ &\quad \left. + \left(\frac{r}{2} A_i - \frac{s}{4} B_i \right) n_{i-1,j} + (\Delta t) p_{i,j} \right] \end{aligned} \right\}. \quad (\text{A19})$$

Eqs. (A18) apply at interior grid points and must be supplemented by upper and lower boundary conditions. These equations are of the same form as (A18) with $a_i = 0$ at the upper boundary and $c_i = 0$ at the lower boundary. Solution of (A18) for each number density requires inversion of a tri-diagonal matrix for which standard routines are available (e.g., Roach, 1972).

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